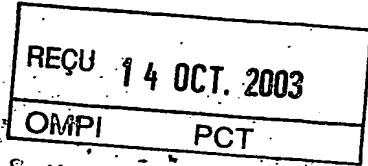




**Europäisches
Patentamt**

**European
Patent Office**

**Office européen
des brevets**



Bescheinigung

Certificate

Attestation

Die angehefteten Unterla-
gen stimmen mit der
ursprünglich eingereichten
Fassung der auf dem näch-
sten Blatt bezeichneten
europäischen Patentanmel-
dung überein.

The attached documents
are exact copies of the
European patent application
described on the following
page, as originally filed.

Les documents fixés à
cette attestation sont
conformes à la version
initialement déposée de
la demande de brevet
européen spécifiée à la
page suivante.

Patentanmeldung Nr. Patent application No. Demande de brevet n°

02405763.0

PRIORITY DOCUMENT
SUBMITTED OR TRANSMITTED IN
COMPLIANCE WITH
RULE 17.1(a) OR (b)

Der Präsident des Europäischen Patentamts;
Im Auftrag

For the President of the European Patent Office

Le Président de l'Office européen des brevets
p.o.

R C van Dijk



Anmeldung Nr:

Application no.: 02405763.0

Demande no:

Anmeldetag:

Date of filing: 04.09.02

Date de dépôt:

Anmelder/Applicant(s)/Demandeur(s):

Ciba Specialty Chemicals Holding Inc.

Klybeckstrasse 141

4057 Basel

SUISSE

Bezeichnung der Erfindung/Title of the invention/Titre de l'invention:

(Falls die Bezeichnung der Erfindung nicht angegeben ist, siehe Beschreibung.

If no title is shown please refer to the description.

Si aucun titre n'est indiqué se référer à la description.)

Method of producing comb copolymers using epoxy-functionalized nitroxylethers

In Anspruch genommene Priorität(en) / Priority(ies) claimed / Priorité(s)
revendiquée(s)

Staat/Tag/Aktenzeichen/State/Date/File no./Pays/Date/Numéro de dépôt:

Internationale Patentklassifikation/International Patent Classification/
Classification internationale des brevets:

C08F/

Am Anmeldetag benannte Vertragsstaaten/Contracting states designated at date of
filing/Etats contractants désignées lors du dépôt:

AT BE BG CH CY CZ DE DK EE ES FI FR GB GR IE IT LI LU MC NL PT SE SK TR

Method of Producing Comb Copolymers Using Epoxy-Functionalized Nitroxylethers

The synthesis of amphiphilic block- and graft copolymers containing both unpolar and polar chain species of different chemical nature has been approached by several techniques. A promising approach for the synthesis of aliphatic polyether backbones has been described by Heitz et al. in Macromol. Chem. 183, 1685 (1982).

One problem, especially in the design of graft copolymers, is the lack of grafting efficiency, especially if a radical "grafting to" process is chosen. Complete grafting of the graft monomer is seldom achieved and hence the final product is always contaminated with homopolymer formed in the grafting step. This process is mostly applied in the synthesis of high impact polystyrene, where styrene is grafted radically onto a polybutadiene latex. More efficient grafting is achieved when active sites within the polymeric backbone are used to covalently attach new polymer chains to the starting molecule. This requires however the presence of well-defined "initiation points" in the backbone.

Linear polyethers based on ethylene oxide and/or propylene oxide, besides their vast application in polyurethanes, find numerous applications in pharmaceutical and biomedical applications. Industrial applications include amongst numerous others flocculating agents in the treatment of industrial waste water, drag reduction and the modification of surface properties, such as the use as antistatic agents. Linear block copolymers of ethylene and propylene oxide also have commercial applications and serve as non-ionic tensides, emulsifiers and stability improvers (as for example "Pluronic®" manufactured by BASF). Also statistical copolymers of this type are accessible. Most of these products are liquids or waxes, depending on their final molecular weight. These copolymers are still water soluble with a minimum content of 25% ethylene oxide and hence pose an interesting class of materials for the synthesis of amphiphilic graft copolymers.

Besides ethylene oxide, propylene oxide and monomers derived therefrom, epichlorohydrine forms polyethers, which are used as specialty rubbers.

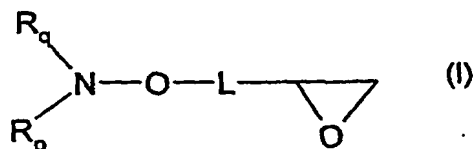
The present invention provides a method of attaching a polymeric side chain to a polymer backbone differing in polarity and chemical structure therefrom and forming a comb polymer structure. This represents a new method in the synthesis of comb copolymers combining two

separate polymerization processes. The properties of polyethers can now be combined with those of typical thermoplastic polymers.

In particular the process provides a method of polymerizing in a first step a polymer backbone from epoxy group containing monomers and in a second step polymerizing under controlled radical conditions a comb structure onto this backbone.

The resulting copolymer structures are of interest in surface modification applications of thermoplastic materials, insuring a permanent polar surface by anchoring the polar moiety via the less polar polymer chains in the matrix of the desired resin. Similarly, these polymers can be used as nonionic surfactants. The incorporation of the novel molecules into a backbone polymer containing epichlorohydrine could lead to rubber-thermoplast comb copolymers.

One aspect of the invention is a method for the preparation of a comb copolymer comprising a) polymerising in a first step one or more epoxy group containing monomers to obtain a polyether, wherein at least one monomer is of formula (I)



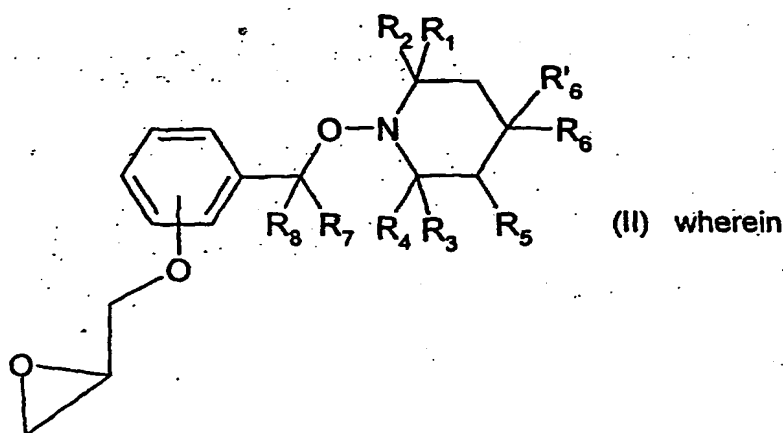
wherein L is a linking group selected from the group consisting of C₁-C₁₈alkylene, phenylene, phenylene-C₁-C₁₈alkylene, C₁-C₁₈alkylene-phenylene, C₁-C₁₈alkylene-phenylene-oxy and C₅-C₁₂cycloalkylene;

R_p and R_q are independently tertiary bound C₄-C₂₈alkyl groups which are unsubstituted or substituted by one or more electron withdrawing groups or by phenyl; or

R_p and R_q together form a 5 or 6 membered heterocyclic ring which is substituted at least by 4 C₁-C₄alkyl groups and which may be interrupted by a further nitrogen or oxygen atom; and in a second step

b) adding to the polymer obtained in step a) at least one ethylenically unsaturated monomer, heating the resulting mixture to a temperature where cleavage of the nitroxylether bond occurs and radical polymerization starts; and polymerizing to the desired degree.

For example the monomer according to formula I is of formula (II)



R_1, R_2, R_3 and R_4 are independently of each other C_1 - C_4 alkyl;

R_5 is hydrogen or C_1 - C_4 alkyl;

R'_6 is hydrogen and R_6 is H, OR_{10} , $NR_{10}R_{11}$, $-O-C(O)-R_{10}$ or $NR_{11}-C(O)-R_{10}$;

R_{10} and R_{11} independently are hydrogen, C_1 - C_{18} alkyl, C_2 - C_{18} alkenyl, C_2 - C_{18} alkynyl or C_2 - C_{18} alkyl which is substituted by at least one hydroxy group or, if R_6 is $NR_{10}R_{11}$, taken together, form a C_2 - C_{12} alkylene bridge or a C_2 - C_{12} alkylene bridge interrupted by at least one O atom; or

R_6 and R'_6 together are both hydrogen, a group $=O$ or $=N-O-R_{20}$ wherein

R_{20} is H, straight or branched C_1 - C_{18} alkyl, C_3 - C_{18} alkenyl or C_3 - C_{18} alkynyl, which may be unsubstituted or substituted, by one or more OH, C_1 - C_8 alkoxy, carboxy, C_1 - C_8 alkoxycarbonyl; C_5 - C_{12} cycloalkyl or C_5 - C_{12} cycloalkenyl;

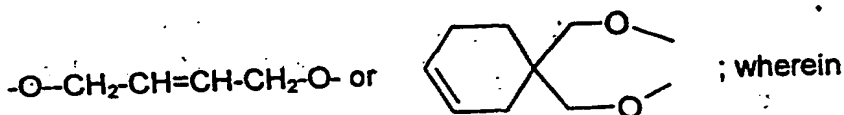
phenyl, C_7 - C_9 phenylalkyl or naphthyl which may be unsubstituted or substituted by one or more C_1 - C_8 alkyl, halogen, OH, C_1 - C_8 alkoxy, carboxy, C_1 - C_8 alkoxycarbonyl;

$-C(O)-C_1$ - C_{38} alkyl, or an acyl moiety of a α, β -unsaturated carboxylic acid having 3 to 5 carbon atoms or of an aromatic carboxylic acid having 7 to 15 carbon atoms;

$-SO_3^-Q^+$, $-PO(O^-Q^+)_2$, $-P(O)(OR_2)_2$, $-SO_2-R_2$, $-CO-NH-R_2$, $-CONH_2$, $COOR_2$, or $Si(Me)_3$, wherein Q^+ is H^+ , ammonium or an alkali metal cation; or

R_6 and R'_6 are independently $-O-C_1$ - C_{12} alkyl, $-O-C_3$ - C_{12} alkenyl, $-O-C_3$ - C_{12} alkynyl, $-O-C_5$ - C_8 cycloalkyl, $-O$ -phenyl, $-O$ -naphthyl, $-O-C_7$ - C_9 phenylalkyl; or

R_6 and R'_6 together form one of the bivalent groups $-O-C(R_{21})(R_{22})-CH(R_{23})-O-$, $-O-CH(R_{21})-CH_{22}-C(R_{22})(R_{23})-O-$, $-O-CH(R_{22})-CH_2-C(R_{21})(R_{23})-O-$, $-O-CH_2-C(R_{21})(R_{22})-CH(R_{23})-O-$, $-O$ -o-phenylene- $O-$, $-O$ -1,2-cyclohexyliden- $O-$,



R_{21} is hydrogen, C_1 - C_{12} alkyl, COOH , $\text{COO-(C}_1\text{-C}_{12})\text{alkyl}$ or $\text{CH}_2\text{OR}_{24}$;

R_{22} and R_{23} are independently hydrogen, methyl ethyl, COOH or $\text{COO-(C}_1\text{-C}_{12})\text{alkyl}$;

R_{24} is hydrogen, C_1 - C_{12} alkyl, benzyl, or a monovalent acyl residue derived from an aliphatic, cycloaliphatic or aromatic monocarboxylic acid having up to 18 carbon atoms; and

R_7 and R_8 are independently hydrogen or C_1 - C_{18} alkyl.

C_1 - C_{18} alkyl can be linear or branched. Examples are methyl, ethyl, propyl, isopropyl, butyl, 2-butyl, isobutyl, t-butyl, pentyl, 2-pentyl, hexyl, heptyl, octyl, 2-ethylhexyl, t-octyl, nonyl, decyl, undecyl, dodecyl or octadecyl. Where up to C_{36} alkyl is possible, C_1 - C_{18} alkyl is preferred.

Alkyl substituted by a group -COOH is for example $\text{CH}_2\text{-COOH}$, $\text{CH}_2\text{-CH}_2\text{-COOH}$, $(\text{CH}_2)_3\text{-COOH}$ or $\text{CH}_2\text{-CHCOOH-CH}_2\text{-CH}_3$

Hydroxyl- or alkoxy carbonyl substituted C_1 - C_{18} alkyl can be, for example, 2-hydroxyethyl, 2-hydroxypropyl, methoxycarbonylmethyl or 2-ethoxycarbonylethyl.

Alkenyl having from 2 to 18 carbon atoms is a branched or unbranched radical, for example propenyl, 2-butenyl, 3-butenyl, isobutenyl, n-2,4-pentadienyl, 3-methyl-2-butenyl, n-2-octenyl, n-2-dodecenyl, isododecenyl.

Alkynyl having from 2 to 18 carbon atoms is a branched or unbranched radical, for example propynyl, 2-butylnyl, 3-butylnyl, isobutylnyl, n-2,4-pentadiynyl, 3-methyl-2-butylnyl, n-2-octynyl, n-2-dodecynyl, isododecynyl.

Examples of alkoxy are methoxy, ethoxy, propoxy, isopropoxy, butoxy, isobutoxy, pentoxy, isopentoxy, hexoxy, heptoxy or octoxy.

C_7 - C_9 phenylalkyl is for example benzyl, α -methylbenzyl, α,α -dimethylbenzyl or 2-phenylethyl, benzyl is preferred.

C₅-C₁₂cycloalkyl is for example cyclopentyl, cyclohexyl, cycloheptyl, methylcyclopentyl or cyclooctyl.

C₅-C₁₂cycloalkenyl is for example 3-cyclopentenyl, 3-cyclohexenyl or 3-cycloheptenyl.

Examples of a monocarboxylic acid having up to 18 carbon atoms are formic acid, acetic acid, propionic acid, the isomers of valeric acid, methyl ethyl acetic acid, trimethyl acetic acid, capronic acid, lauric acid or stearic acid. Examples for unsaturated aliphatic acids are acrylic acid, methacrylic acid, crotonic acid, linolic acid and oleic acid.

Typical examples of cycloaliphatic carboxylic acids are cyclohexane carboxylic acid or cyclopentane carboxylic acid.

Examples of aromatic carboxylic acids are benzoic acid, salicylic acid or cinnamic acid.

Halogen is F, Cl, Br or I.

C₁-C₁₈alkylene is a branched or unbranched radical, for example methylene, ethylene, propylene, trimethylene, tetramethylene, pentamethylene, hexamethylene, heptamethylene, octamethylene, decamethylene or dodecamethylene.

C₂-C₁₂alkylene bridges interrupted by at least one O atom are, for example, -CH₂-O-CH₂-CH₂-, -CH₂-O-CH₂-CH₂-CH₂-, -CH₂-O-CH₂-CH₂-CH₂-CH₂-, -CH₂-O-CH₂-CH₂-O-CH₂-.

Alkoxy carbonyl is for example methoxycarbonyl, ethoxycarbonyl, propoxycarbonyl.

Preferably R₁, R₂, R₃, R₄ are methyl, or R₁ and R₃ are ethyl and R₂ and R₄ are methyl, or R₁ and R₂ are ethyl and R₃ and R₄ are methyl.

For instance R₅ is hydrogen or methyl.

In particular R₆ is hydrogen and R₈ is H, OR₁₀, NR₁₀R₁₁, -O-C(O)-R₁₀ or NR₁₁-C(O)-R₁₀; R₁₀ and R₁₁ independently are hydrogen, C₁-C₁₈alkyl, C₂-C₁₈alkenyl, C₂-C₁₈alkinyl or C₂-C₁₈alkyl which is substituted by at least one hydroxy group or, if R₈ is NR₁₀R₁₁, taken

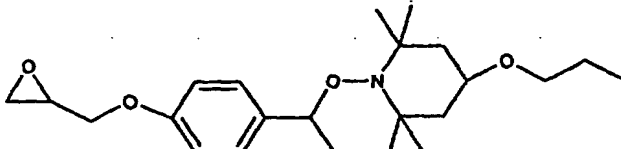
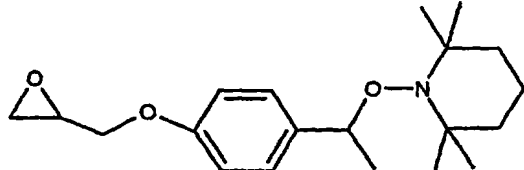
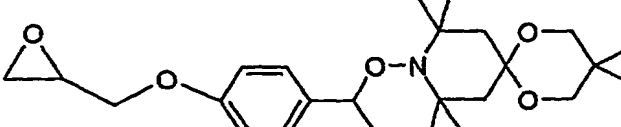
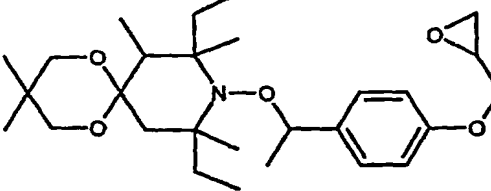
together, form a C_2-C_{12} alkylene bridge or a C_2-C_{12} alkylene bridge interrupted by at least one O atom; or

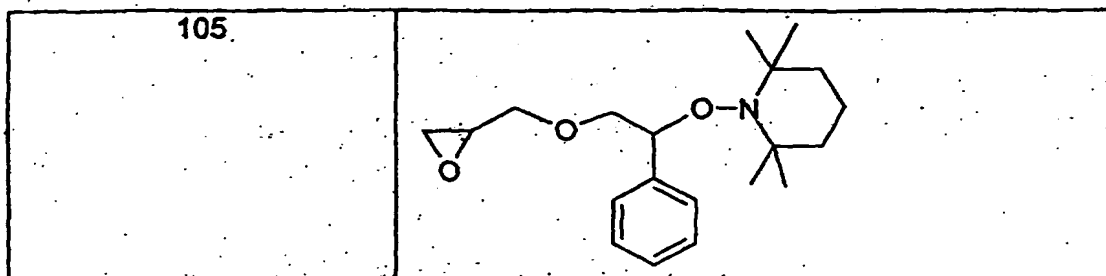
R_8 and R'_8 together are both hydrogen, a group $=O$ or $=N-O-R_{20}$ wherein R_{20} is H or straight or branched C_1-C_{18} alkyl.

In another preferred embodiment of the invention R_8 and R'_8 together form one of the bivalent groups $-O-C(R_{21})(R_{22})-CH(R_{23})-O-$, $-O-CH(R_{21})-CH_2-C(R_{22})(R_{23})-O-$, $-O-CH(R_{22})-CH_2-C(R_{21})(R_{23})-O-$, $-O-CH_2-C(R_{21})(R_{22})-CH(R_{23})-O-$ and R_{21} , R_{22} and R_{23} have the meaning as defined above.

Specific compounds are given in Table A

Table A

Compound Number	Structure
101	
102	
103	
104	



The compounds of formula II and in particular the compounds given in Table A are known and may be prepared as described in WO 99/46261, WO 02/48109 or US 5 721 320.


Examples of suitable other epoxy functional monomers  which can be used as comonomers are given in Table B.

Table B

Name	CAS No.	X
Ethylene oxide	75-21-8	H
Propylene oxide	75-56-9	CH ₃
2,3-Epoxypropyl-phenylether	122-60-1	CH ₂ -O-C ₆ H ₅
2,3-Epoxypropyl-4-nonyl-phenylether	6178-32-1	CH ₂ -O-C ₆ H ₅ -C ₉ H ₁₉
Epichlorohydrine	106-89-8	-CH ₂ -Cl
2,3-Epoxypropyl-2,2,3,3,4,4,5,5-octafluoropentylether	19932-27-5	CH ₂ -O-CH ₂ -(CF ₂) ₃ CHF ₂

For instance the epoxy group containing a monomer different from that of formula II is selected from the group consisting of ethylene oxide, propylene oxide, 2,3-epoxypropyl-phenylether, 2,3-epoxypropyl-4-nonyl-phenylether, epichlorohydrine and 2,3-epoxypropyl-2,2,3,3,4,4,5,5-octafluoropentylether.

These compounds are known and commercially available.

Preferably the weight ratio of monomer of formula I or formula II to the sum of other monomers is from 99:1 to 1:99, particularly 80:20 to 20:80, specifically 75:25 to 25:75.

The general polymerization procedure of step a) is well known and for example described in Encyclopedia of Polymer Science and Technology, Vol 6, 1967, 103-209.

There are principally two different processes. The first depends upon the tendency of the oxiran group to oxyalkylated active-hydrogen-sites in the presence of Lewis acids or Lewis bases as catalysts. The second type of polymerization reaction involves the rapid polymerization of the oxiran group to high molecular weight polymers on a catalytic surface in a heterogeneous reaction system. Other initiation systems are described in Odian, "Principles of polymerization", Wiley-Interscience New York, 1991, pp.536 and Houben Weyl, Makromolekulare Stoffe, Bd. E20/2, Thieme Stuttgart, 1987, pp 1367. They include furthermore aluminium porphyrin compounds and certain iron and zinc complexes as catalysts.

The polymerization can be carried out in bulk or in solution, containing 10-90% (by vol.) solvent, the latter especially if gaseous monomers (propylene oxide or ethylene oxide) are used. Suitable solvents include tetrahydrofuran (THF), benzene, toluene, acetonitrile, dimethylformamide (DMF), chlorinated solvents and mixtures thereof. If the backbone contains a high fraction of ethylene oxide, also water or mixtures of water with suitable organic solvents can be used.

Suitable Lewis bases are for example alkali metal alcoholates.

The polyether polymer of step a) has for example an average weight molecular weight of M_w 1000 to 100 000, preferably from 2000 to 50 000.

The reaction temperature should be kept preferably as low as possible since cleavage of the nitroxylether bond may occur at temperatures above 100° C. The polymerization temperature should therefore not exceed 100° C. A suitable polymerization temperature is for example from 10° to 80° C, preferably from 30° to 70° C. Polymerization is normally carried out under inert gas atmosphere at normal atmospheric pressure.

Since lower reaction temperatures are applied reaction time is usually longer, typically from 1-72 hours, in particular 1-48 hours, preferably 2-24 hours.

The isolation of the polyether backbone polymer depends on its molecular structure. Residual monomer can be removed in vacuo at temperatures not exceeding 100°C if they are liquid, extracted (for example via Soxhlet extraction) or washed with appropriate solvents if they are solid.

Preferably the ethylenically unsaturated monomer or oligomer added in step b) is selected from the group consisting of ethylene, propylene, n-butylene, i-butylene, styrene, substituted styrene, conjugated dienes, acrolein, vinyl acetate, vinylpyrrolidone, vinylimidazole, maleic anhydride, (alkyl)acrylic acid anhydrides, (alkyl)acrylic acid salts, (alkyl)acrylic esters, (meth)acrylonitriles, (alkyl)acrylamides, vinyl halides or vinylidene halides.

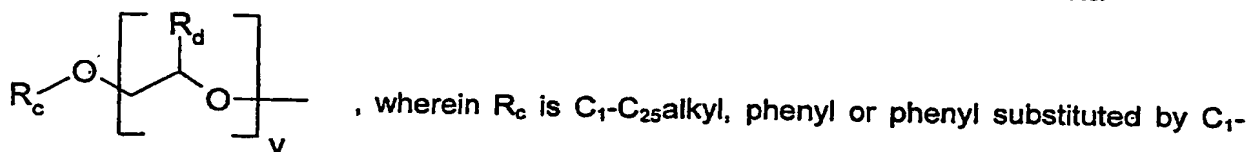
Particularly the ethylenically unsaturated monomers are ethylene, propylene, n-butylene, i-butylene, isoprene, 1,3-butadiene, α -C₅-C₁₈alkene, styrene, α -methyl styrene, p-methyl styrene or a compound of formula $\text{CH}_2=\text{C}(\text{R}_a)-(\text{C}=\text{Z})-\text{R}_b$, wherein R_a is hydrogen or C₁-C₄alkyl, R_b is NH₂, O⁻(Me⁺), glycidyl, unsubstituted C₁-C₁₈alkoxy, C₂-C₁₀₀alkoxy interrupted by at least one N and/or O atom, or hydroxy-substituted C₁-C₁₈alkoxy, unsubstituted C₁-C₁₈alkylamino, di(C₁-C₁₈alkyl)amino, hydroxy-substituted C₁-C₁₈alkylamino or hydroxy-substituted di(C₁-C₁₈alkyl)amino, -O-CH₂-CH₂-N(CH₃)₂ or -O-CH₂-CH₂-N⁺H(CH₃)₂ An⁻;

An⁻ is a anion of a monovalent organic or inorganic acid;

Me is a monovalent metal atom or the ammonium ion.

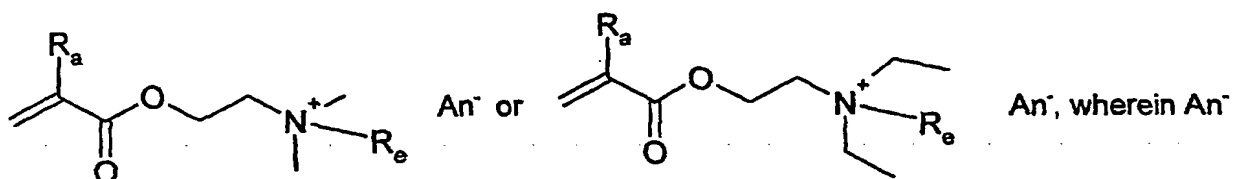
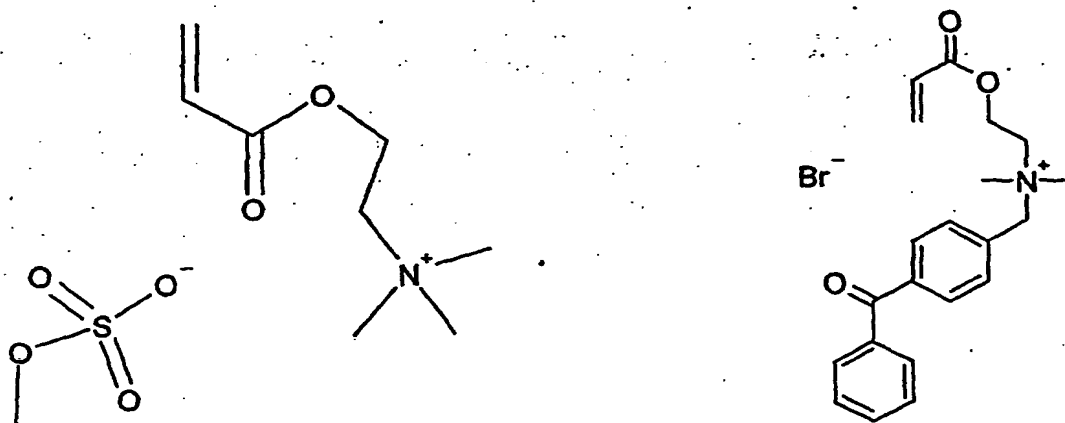
Z is oxygen or sulfur.

Examples for R_a as C₂-C₁₀₀alkoxy interrupted by at least one O atom are of formula

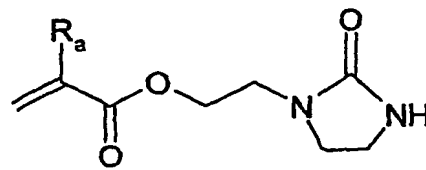
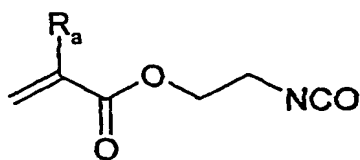
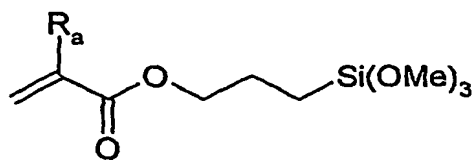
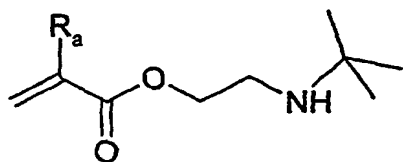
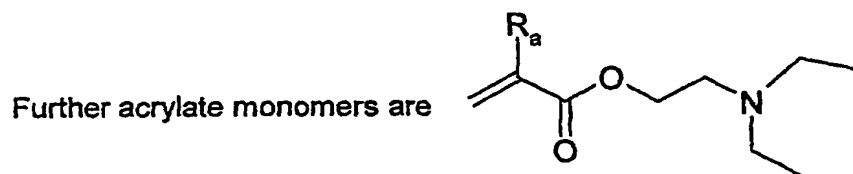


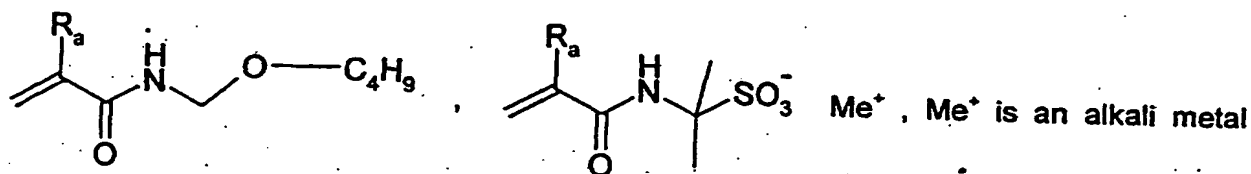
C₁₈alkyl, R_d is hydrogen or methyl and v is a number from 1 to 50. These monomers are for example derived from non ionic surfactants by acrylation of the corresponding alkoxyated alcohols or phenols. The repeating units may be derived from ethylene oxide, propylene oxide or mixtures of both.

Further examples of suitable acrylate or methacrylate monomers are given below.

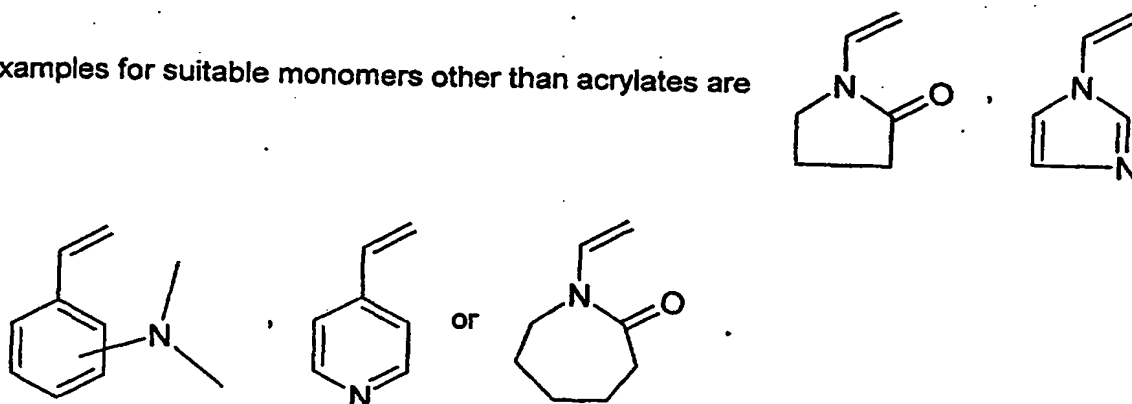


and R_a have the meaning as defined above and R_g is methyl, benzyl or benzoylbenzyl. An^- is preferably Cl^- , Br^- or $^-\text{O}_3\text{S}-\text{O}-\text{CH}_3$.





Examples for suitable monomers other than acrylates are



Preferably R_a is hydrogen or methyl, R_b is NH_2 , glycidyl, unsubstituted or with hydroxy substituted $\text{C}_1\text{-C}_4$ alkoxy, unsubstituted $\text{C}_1\text{-C}_4$ alkylamino, di($\text{C}_1\text{-C}_4$ alkyl)amino, hydroxy-substituted $\text{C}_1\text{-C}_4$ alkylamino or hydroxy-substituted di($\text{C}_1\text{-C}_4$ alkyl)amino; and Z is oxygen.

Particularly preferred ethylenically unsaturated monomers are styrene, methylacrylate, ethylacrylate, butylacrylate, isobutylacrylate, tert. butylacrylate, hydroxyethylacrylate, hydroxypropylacrylate, dimethylaminoethylacrylate, glycidylacrylates, methyl(meth)acrylate, ethyl(meth)acrylate, butyl(meth)acrylate, hydroxyethyl(meth)acrylate, hydroxypropyl(meth)acrylate, dimethylaminoethyl(meth)acrylate, glycidyl(meth)acrylates, acrylonitrile, acrylamide, methacrylamide or dimethylaminopropyl-methacrylamide.

For example the weight ratio between the polyether prepared in step a) and the ethylenically unsaturated monomer added in step b) is from 90:10 to 10:90.

As already mentioned the nitroxylether bond cleaves at elevated temperature and radical polymerization is initiated. Preferably in step b) the polymerization temperature is from 80°C to 160°C , in particular from 100°C to 140°C .

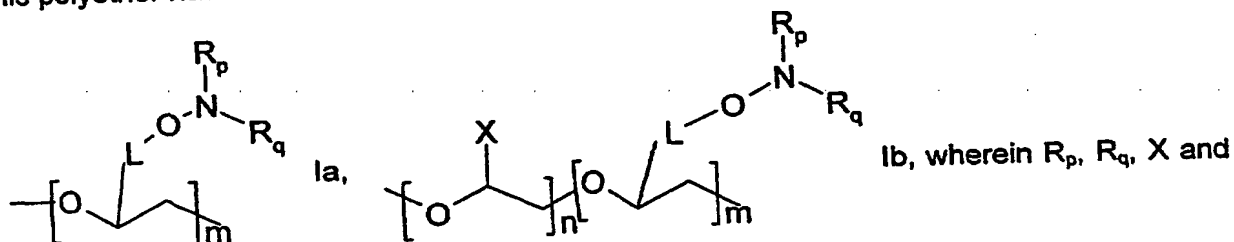
Typically the average weight molecular weight M_w is from 2000 to 300 000, preferably from 3000 bis 100000.

The polydispersity index of the resulting comb copolymer is typically between 1.1 and 3.0.

A further aspect of the invention is a composition comprising a compound of formula II as defined above, at least one epoxy functional monomer different from that of formula II and optional water or an organic solvent or mixtures thereof.

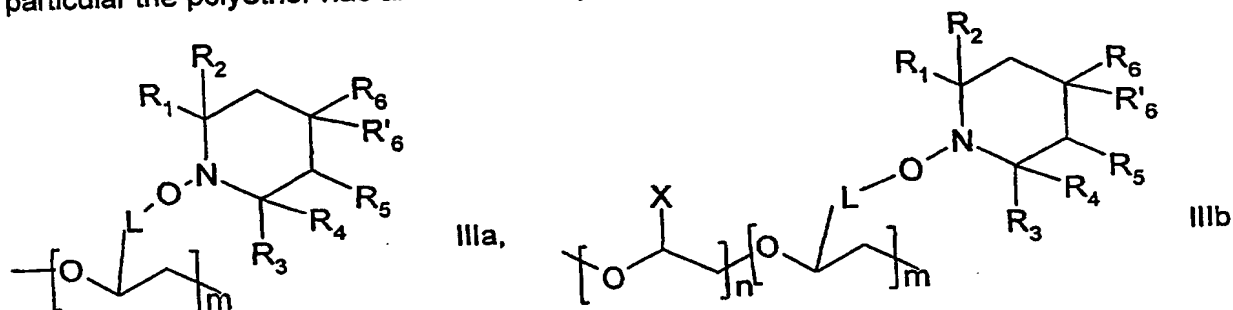
Yet another aspect of the invention is a polyether obtainable according to step a) of the method described above.

This polyether has an idealized repetitive structural element of formula Ia or Ib



L are as defined above and n and m are independently a number from 10 to 1000.

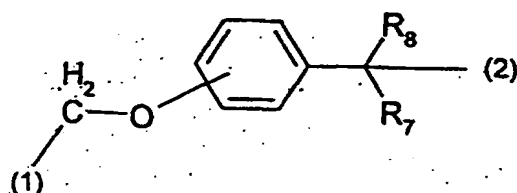
In particular the polyether has an idealized repetitive structural element of formula IIIa or IIIb



wherein R_1 , R_2 , R_3 , R_4 , R_5 , R_6 , R'_6 and L are as defined above, m and n are independently a number from 10 to 1000 and

X is H, CH_3 , $CH_2-O-C_6H_5$, $CH_2-O-C_6H_5-C_9H_{19}$, CH_2Cl or $CH_2-O-CH_2-(CF_2)_3CHF_2$.

Most preferably L is a bivalent linking group of formula



wherein (1) denotes the bond to the polymer

backbone and (2) denotes the bond to the oxygen atom of the nitroxyl radical; R₇ and R₈ are as defined above.

Further subjects of the invention are a comb copolymer obtainable according to the method as described above and the use of a polyether with pending nitroxylether groups for the preparation of a comb copolymer.

For instance the ethylenically unsaturated monomer forming the comb is selected from the group consisting of styrene, substituted styrene, (alkyl)acrylic acidanhydrides, (alkyl)acrylic acid salts, (alkyl)acrylic esters, (meth)acrylonitriles and (alkyl)acrylamides.

Definitions for the individual substituents have already been given for the method of preparation of comb copolymers, they apply also to the other aspects of the invention.

The polymers prepared by the present invention are useful for following applications:

adhesives, detergents, dispersants, emulsifiers, surfactants, defoamers, adhesion promoters, corrosion inhibitors, viscosity improvers, lubricants, rheology modifiers, thickeners, crosslinkers, paper treatment, water treatment, electronic materials, paints, coatings, photography, ink materials, imaging materials, superabsorbants, cosmetics, hair products, preservatives, biocide materials or modifiers for asphalt, leather, textiles, ceramics and wood.

Because the polymerization of step b) is a "living" polymerization, it can be started and stopped practically at will. Furthermore, the polymer product retains the functional alkoxyamine group allowing a continuation of the polymerization in a living matter. Thus, in one embodiment of this invention, once the first monomer is consumed in the initial radical polymerizing step a second monomer can then be added to form a second block on the growing polymer chain in a second polymerization step. Therefore it is possible to carry out additional polymerizations with the same or different monomer(s) to prepare multi-block copolymers.

Furthermore, since this is a radical polymerization, blocks can be prepared in essentially any order. One is not necessarily restricted to preparing block copolymers where the sequential polymerizing steps must flow from the least stabilized polymer intermediate to the most stabilized polymer intermediate, such as is the case in ionic polymerization. Thus it is possible to prepare a multi-block copolymer in which a polyacrylonitrile or a poly(meth)acrylate block is prepared first, then a styrene or butadiene block is attached thereto, and so on.

Random copolymers and tapered copolymer structures can be synthesized as well by using a mixture of monomers or adding a second monomer before the first one is consumed.

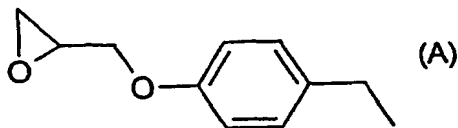
Yet another aspect of the invention is the use of a comb copolymer obtainable according to the method described above as adhesive, surface modifier, surfactant or compatibilizer in thermoplastic, elastic or thermosetting polymers.

The following examples illustrate the invention.

Examples (V1 and V2) prove the polymerizability of the epoxy group

Compound A is the precursor molecule in the synthesis for the epoxy-group containing nitroxyl ethers.

Compound A is known and prepared according to standard methods.



In order to test its principal ability of polymerizing under Lewis base catalysis compound A is subjected to an anionic polymerization using potassium - *tert.* - butylate.

In a dry, Argon-purged Schlenk tube equipped with a rubber septum, a magnetic stir bar and an Argon inlet, 3.56 g (0.02 mol) compound A (liquid) are dissolved in 5 ml dry toluene (Merck). 210 mg (1.82 mmol) potassium - *tert.* - butylate are added and the homogeneous solution is heated for 6 hours at 110°C. After cooling to room temperature, 2 ml of methanol

are added via syringe and subsequently the solvents are removed in vacuo. The product is obtained as a colorless wax (V1).

NMR analysis confirms the formation of a polyether due to the presence of the characteristic signals $\text{-O-CH}_2\text{-CH-}$. Furthermore the absence of monomer is confirmed.

Molecular weights are determined by GPC in tetrahydrofuran (THF) on a HP 1090 device equipped with an RI and UV detector, using a solvent flow of 1 ml/min. Columns are calibrated using polystyrene standards.

The same experiment is successfully repeated with 1 mmol potassium - *tert.* - butylate as Initiator (V2). Table 1 lists polymer yields and molecular weight data. The "living nature" of this type of polymerization is confirmed by the different molecular weights obtained when using different amounts of initiator.

Table 1

Example	Conversion Compound A (%)	M_n (calc.)	M_n (GPC)	M_w	M_w/M_n
V1	92	1840	2500	3900	1.58
V2	82	3280	3500	6600	1.88

Example E1-E7: Preparation of the polyether backbone polymer with pending nitroxylether groups

Example E1

In a dry, Argon-purged Schlenk tube equipped with a rubber septum, a magnetic stir bar and an Argon inlet, 40 g (0.1 mol) compound 101 (light brown oil), 30 g (0.18 mol) compound A and 4 g (0.036 mol) potassium - *tert.* - butylate are dissolved in 100 ml dry toluene. The light yellow solution is heated at 60°C for 18 hours. After the addition of 2 ml methanol solvents are removed in vacuo and the product is dried overnight in vacuo at room temperature. The product is obtained as a highly viscous brown oil.

Example E2

In a dry, Argon-purged Schlenk tube equipped with a rubber septum, a magnetic stir bar and an Argon inlet, 20 g (0.05 mol) compound 101 (light brown oil), 30 g (0.18 mol) compound A

and 4 g (0.036 mol) potassium - tert. - butylate are dissolved in 100 ml dry toluene. The light yellow solution is heated at 60°C for 18 hours). After the addition of 1 ml methanol solvents are removed in vacuo and the product dried overnight in at room temperature. The product is obtained as a viscous yellow oil.

Example E3

In a dry, Argon-purged Schlenk tube equipped with a rubber septum, a magnetic stir bar and an Argon inlet, 3.35 g (0.01 mol) compound 102 (colorless oil), 7.12 g (0.04 mol) compound A and 0.41 g (0.0036 mol) potassium - tert. - butylate are dissolved in 10 ml dry toluene. The solution is heated at 80°C for 6 hours. After the addition of 1 ml methanol, solvents are removed in vacuo and the product dried overnight in at room temperature. The product is obtained as very viscous yellow oil.

Example E4

In a dry, Argon-purged Schlenk tube equipped with a rubber septum, a magnetic stir bar and an Argon inlet, 3.35 g (0.01 mol) compound 102 (colorless oil), 3.56 g (0.02 mol) compound A and 0.41 g (0.0036 mol) potassium - tert. - butylate are dissolved in 10 ml dry toluene. The solution is heated at 80°C for 6 hours. After the addition of 1 ml methanol, solvents are removed in vacuo and the product dried overnight in at room temperature. The product is obtained as light yellow oil.

Example E5

In a dry, Argon-purged Schlenk tube equipped with a rubber septum, a magnetic stir bar and an Argon inlet, 17 g (0.051 mol) compound 102 (colorless oil), 14 g (0.051 mol) 2,3-epoxypropyl-4-nonylphenylether (techn., Sigma-Aldrich, CAS # 6178-32-1) and 1 g (0.009 mol) potassium - tert. - butylate are dissolved in 60 ml dry toluene. The solution is heated at 60°C for 6 hours. After the addition of 1 ml methanol, solvents are removed in vacuo and the product dried overnight in at room temperature. The product is obtained as a light brown oil.

Example E6

In a dry, Argon-purged Schlenk tube equipped with a rubber septum, a magnetic stir bar and an Argon inlet, 17 g (0.051 mol) compound 102 (colorless oil), 7 g (0.025 mol) 2,3-epoxypropyl-4-nonylphenylether and 1 g (0.009 mol) potassium - tert. - butylate are dissolved in 60 ml dry toluene. The solution is heated at 60°C for 6 hours. After the addition of 1 ml

methanol, solvents are removed in vacuo and the product dried overnight in at room temperature. The product is obtained as a light brown oil.

Example E7

In a dry, Argon-purged Schlenk tube equipped with a rubber septum, a magnetic stir bar and an Argon inlet, 17 g (0.0 mol) compound 102 (colorless oil), 28 g (0.101 mol) epoxypropyl-4-nonylphenylether and 1 g (0.009 mol) potassium - tert. - butylate are dissolved in 60 ml dry toluene. The solution is heated at 60°C for 6 hours. After the addition of 1 ml methanol, solvents are removed in vacuo and the product dried overnight in at room temperature. The product is obtained as brown oil.

Table 2 summarizes the yields and the molecular weight data of the obtained products. Polymer yield is determined gravimetrically after drying of the products.

Table 2: Molecular weights and conversion data

Example	Polymer yield (%)	M_n (GPC)	M_w	M_w/M_n
E1	97	3500	7500	2.08
E2	97	2500	5000	2.00
E3	98	4500	12400	2.70
E4	99	2900	7600	2.63
E 5	not determined	2500	3700	1.46
E 6	n.d.	2300	3000	1.33
E 7	n.d.	2500	3300	1.31

Preparation of comb copolymers by reinitiation

Example E8

In a dry Schlenk tube equipped with a stopcock, magnetic stirbar and an Argon inlet, 5 g of the polymer of example E5 are dissolved in 50 g (mol) of freshly distilled styrene (Merck). The solution is degassed by three consecutive freeze-thaw cycles and purged with argon. The tube is then immersed in an oil bath a heated at 130°C for 6 hours. After cooling to room temperatures, volatiles are removed in vacuo and the crude reaction product is analyzed by GPC. The graft copolymer yield is determined gravimetrically.

Example E9

In a dry Schlenk tube equipped with a stopcock, magnetic stirbar and an Argon inlet, 5 g of the polymer of example E6 are dissolved in 50 g (mol) of freshly distilled styrene (Merck). The solution is degassed by three consecutive freeze-thaw cycles and purged with argon. The tube is then immersed in an oil bath and heated at 130°C for 6 hours. After cooling to room temperatures, volatiles are removed in vacuo and the crude reaction product is analyzed by GPC. The graft copolymer yield is determined gravimetrically.

Example E10

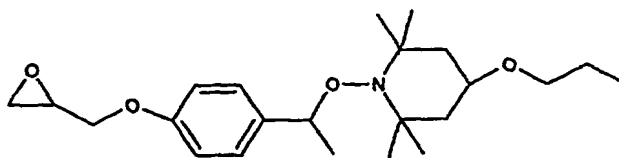
In a dry Schlenk tube equipped with a stopcock, magnetic stirbar and an Argon inlet, 5 g of the polymer of example E7 are dissolved in 50 g (mol) of freshly distilled styrene (Merck). The solution is degassed by three consecutive freeze-thaw cycles and purged with argon. The tube is then immersed in an oil bath and heated at 130°C for 6 hours. After cooling to room temperatures, volatiles are removed in vacuo and the crude reaction product is analyzed by GPC. The graft copolymer yield is determined gravimetrically.

Table 3 summarizes the yields and the molecular weight data of the obtained graft copolymers. Molecular weights are determined as described above.

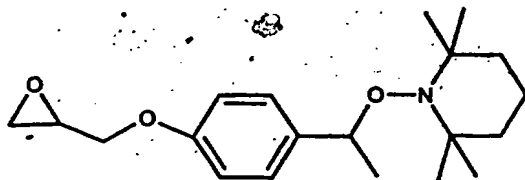
Table 3: Molecular weights and styrene monomer conversion

Example	% styrene grafted onto backbone	M_n (GPC)	M_w	M_w/M_n
E 8	22	4600	6500	1.42
E 9	7	4100	5600	1.38
E 10	15	3700	8700	2.33

Compound 101



Compound 102

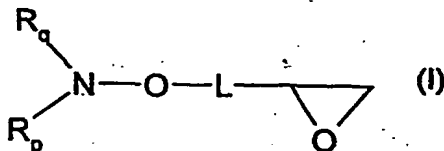


Both compounds are prepared according to WO 99/46261, examples A1 and A5.

Claims

1. Method for the preparation of a comb copolymer comprising

a) polymerising in a first step one or more epoxy group containing monomers to obtain a polyether, wherein at least one monomer is of formula (I)



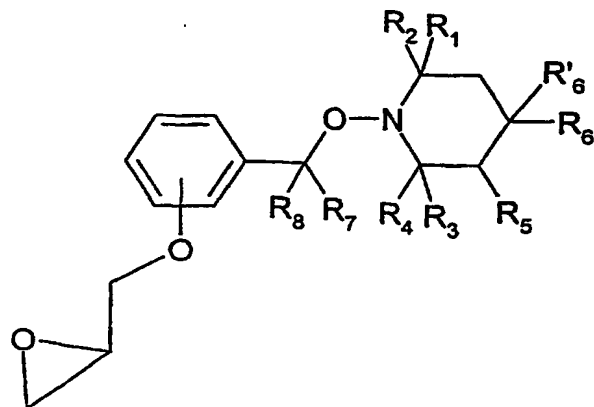
wherein L is a linking group selected from the group consisting of C₁-C₁₈alkylene, phenylene, phenylene-C₁-C₁₈alkylene, C₁-C₁₈alkylene-phenylene, C₁-C₁₈alkylene-phenylene-oxy and C₅-C₁₂cycloalkylene;

R_p and R_q are independently tertiary bound C₄-C₂₈alkyl groups which are unsubstituted or substituted by one or more electron withdrawing groups or by phenyl; or

R_p and R_q together form a 5 or 6 membered heterocyclic ring which is substituted at least by 4 C₁-C₄alkyl groups and which may be interrupted by a further nitrogen or oxygen atom; and in a second step

b) adding to the polymer obtained in step a) at least one ethylenically unsaturated monomer, heating the resulting mixture to a temperature where cleavage of the nitroxylether bond occurs and radical polymerization starts; and polymerizing to the desired degree.

2. A process according to claim 1 wherein the monomer is of formula (II)



(II) wherein

R₁, R₂, R₃ and R₄ are independently of each other C₁-C₄alkyl;
R₅ is hydrogen or C₁-C₄alkyl;

R'_8 is hydrogen and R_8 is H, OR_{10} , $NR_{10}R_{11}$, $-O-C(O)-R_{10}$ or $NR_{11}-C(O)-R_{10}$;

R_{10} and R_{11} independently are hydrogen, C_1-C_{18} alkyl, C_2-C_{18} alkenyl, C_2-C_{18} alkinyl or C_2-C_{18} alkyl which is substituted by at least one hydroxy group or, if R_8 is $NR_{10}R_{11}$, taken together, form a C_2-C_{12} alkylene bridge or a C_2-C_{12} alkylene bridge interrupted by at least one O atom; or

R_8 and R'_8 together are both hydrogen, a group $=O$ or $=N-O-R_{20}$ wherein

R_{20} is H, straight or branched C_1-C_{18} alkyl, C_3-C_{18} alkenyl or C_3-C_{18} alkinyl, which may be unsubstituted or substituted, by one or more OH, C_1-C_8 alkoxy, carboxy, C_1-C_8 alkoxycarbonyl, C_5-C_{12} cycloalkyl or C_5-C_{12} cycloalkenyl;

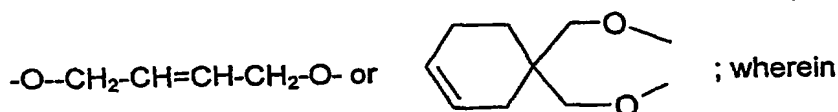
phenyl, C_7-C_9 phenylalkyl or naphthyl which may be unsubstituted or substituted by one or more C_1-C_8 alkyl, halogen, OH, C_1-C_8 alkoxy, carboxy, C_1-C_8 alkoxycarbonyl;

$-C(O)-C_1-C_{36}$ alkyl, or an acyl moiety of a α,β -unsaturated carboxylic acid having 3 to 5 carbon atoms or of an aromatic carboxylic acid having 7 to 15 carbon atoms;

$-SO_3^-Q^+$, $-PO(O^-Q^+)_2$, $-P(O)(OR_2)_2$, $-SO_2-R_2$, $-CO-NH-R_2$, $-CONH_2$, $COOR_2$, or $Si(Me)_3$, wherein Q^+ is H^+ , ammonium or an alkali metal cation; or

R_8 and R'_8 are independently $-O-C_1-C_{12}$ alkyl, $-O-C_3-C_{12}$ alkenyl, $-O-C_3-C_{12}$ alkinyl, $-O-C_5-C_8$ cycloalkyl, $-O$ -phenyl, $-O$ -naphthyl, $-O-C_7-C_9$ phenylalkyl; or

R_8 and R'_8 together form one of the bivalent groups $-O-C(R_{21})(R_{22})-CH(R_{23})-O-$, $-O-CH(R_{21})-CH_2-C(R_{22})(R_{23})-O-$, $-O-CH(R_{22})-CH_2-C(R_{21})(R_{23})-O-$, $-O-CH_2-C(R_{21})(R_{22})-CH(R_{23})-O-$, $-O$ -o-phenylene- $O-$, $-O$ -1,2-cyclohexyliden- $O-$,



R_{21} is hydrogen, C_1-C_{12} alkyl, $COOH$, $COO-(C_1-C_{12})$ alkyl or CH_2OR_{24} ;

R_{22} and R_{23} are independently hydrogen, methyl ethyl, $COOH$ or $COO-(C_1-C_{12})$ alkyl;

R_{24} is hydrogen, C_1-C_{12} alkyl, benzyl, or a monovalent acyl residue derived from an aliphatic, cycloaliphatic or aromatic monocarboxylic acid having up to 18 carbon atoms; and

R_7 and R_8 are independently hydrogen or C_1-C_{18} alkyl.

3. A method according to claim 2 wherein R_1 , R_2 , R_3 , R_4 are methyl, or R_1 and R_3 are ethyl and R_2 and R_4 are methyl, or R_1 and R_2 are ethyl and R_3 and R_4 are methyl.

4. A method according to claim 2 wherein R_5 is hydrogen or methyl.

5. A method according to claim 2 wherein

R'_6 is hydrogen and R_6 is H, OR_{10} , $NR_{10}R_{11}$, $-O-C(O)-R_{10}$ or $NR_{11}-C(O)-R_{10}$.

R_{10} and R_{11} independently are hydrogen, C_1-C_{18} alkyl, C_2-C_{18} alkenyl, C_2-C_{18} alkinyl or C_2-C_{18} alkyl which is substituted by at least one hydroxy group or, if R_6 is $NR_{10}R_{11}$, taken together, form a C_2-C_{12} alkylene bridge or a C_2-C_{12} alkylene bridge interrupted by at least one O atom; or

R_6 and R'_6 together are both hydrogen, a group $=O$ or $=N-O-R_{20}$ wherein

R_{20} is H or straight or branched C_1-C_{18} alkyl.

6. A method according to claim 2 wherein

R_6 and R'_6 together form one of the bivalent groups $-O-C(R_{21})(R_{22})-CH(R_{23})-O-$, $-O-CH(R_{21})-CH_2-C(R_{22})(R_{23})-O-$, $-O-CH(R_{22})-CH_2-C(R_{21})(R_{23})-O-$, $-O-CH_2-C(R_{21})(R_{22})-CH(R_{23})-O-$ and R_{21} , R_{22} and R_{23} have the meaning as defined in claim 2.

7. A method according to claim 1 wherein the epoxy group containing monomer different from formula II is selected from the group consisting of ethylene oxide, propylene oxide, 2,3-epoxypropyl-phenylether, 2,3-epoxypropyl-4-nonyl-phenylether, epichlorohydrine and 2,3-epoxypropyl-2,2,3,3,4,4,5,5-octafluoropentylether.

8. A method according to claim 1 wherein in Stepp a) the weight ratio of the monomer of formula I to the sum of the other monomers is from 99:1 to 1:99.

9. A method according to claim 1 wherein in step b) the ethylenically unsaturated monomer or oligomer is selected from the group consisting of ethylene, propylene, n-butylene, i-butylene, styrene, substituted styrene, conjugated dienes, acrolein, vinyl acetate, vinylpyrrolidone, vinylimidazole, maleic anhydride, (alkyl)acrylic acidanhydrides, (alkyl)acrylic acid salts, (alkyl)acrylic esters, (meth)acrylonitriles, (alkyl)acrylamides, vinyl halides and vinylidene halides.

10. A method according to claim 9 wherein in step b) the ethylenically unsaturated monomers are styrene, methylacrylate, ethylacrylate, butylacrylate, isobutylacrylate, tert. butylacrylate, hydroxyethylacrylate, hydroxypropylacrylate, dimethylaminoethylacrylate, glycidylacrylates, methyl(meth)acrylate, ethyl(meth)acrylate, butyl(meth)acrylate, hydroxyethyl(meth)acrylate, hydroxypropyl(meth)acrylate, dimethylaminoethyl(meth)acrylate,

glycidyl(meth)acrylates, acrylonitrile, acrylamide, methacrylamide or dimethylaminopropyl-methacrylamide.

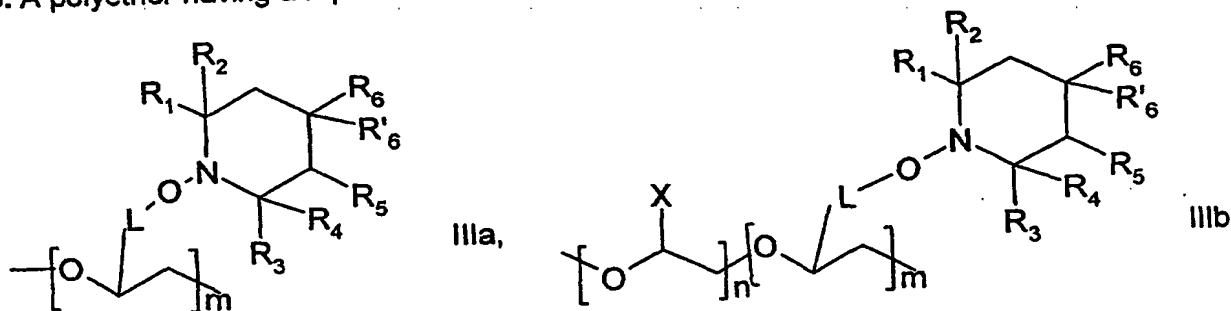
11. A method according to claim 1 wherein in step b) the weight ratio between the polyether prepared in step a) and the ethylenically unsaturated monomer is from 90:10 to 10:90.

12. A method according to claim 1 wherein in step b) the polymerization temperature is from 80° C to 160° C.

13. A composition comprising a compound of formula II as defined in claim 2, at least one epoxy functional monomer different from that of formula II and optional water or an organic solvent or mixtures thereof.

14. A polyether obtainable according to step a) of the method of claim 1.

15. A polyether having a repetitive structural element of formula IIIa or IIIb



wherein R_1 , R_2 , R_3 , R_4 , R_5 , R_6 , R'_6 and L are as defined above, m and n are number from 10 to 1000 and

X is H , CH_3 , $CH_2-O-C_6H_5$, $CH_2-O-C_6H_5-C_9H_{19}$, $-CH_2Cl$ or $CH_2-O-CH_2-(CF_2)_3CHF_2$.

16. A comb copolymer obtainable according to the method of claim 1.

17. A comb polymer according to claim 16 wherein the ethylenically unsaturated monomer forming the comb is selected from the group consisting of styrene, substituted styrene, (alkyl)acrylic acidanhydrides, (alkyl)acrylic acid salts, (alkyl)acrylic esters, (meth)acrylonitriles and (alkyl)acrylamides.

18. Use of a polyether with pending nitroxylether groups according to claim 15 for the preparation of a comb copolymer.

19. Use of a comb copolymer obtainable according to the method of claim 1 as adhesive, surface modifier, surfactant or compatibilizer in thermoplastic, elastic or thermosetting polymers.

Abstract

The present invention provides a method of attaching a polymeric side chain differing in polarity and chemical structure from the backbone and forming a comb polymer structure. In particular the process provides a method of polymerizing in a first step a polymer backbone from epoxy group containing monomers and in a second step polymerizing under controlled radical conditions a comb structure onto this backbone.

PCT Application
EP0309410

